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Spectral Measurements of Ocean-Dumped Wastes Tested in the Marine Upwelled Spectral Signature Laboratory

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Scientific and Technical Information Branch

## SUMMARY

Spectral reflectance characteristics of waste from two industrial plants, the American Cyanamid plant and the Du Pont (Graselli) plant, in Linden, New Jersey, and from a consortium of pharmaceutical plants in Puerto Rico were measured in the laboratory. The wastes (concentrate) had total suspended solids of 465 ppm, 67.8 ppm, and 7340 ppm, respectively. Various mixtures of the wastes were tested in a base of artificial seawater. All of the materials formed precipitates when added to the seawater. The test mixtures contained up to 29.9 ppm of total suspended solids for the American Cyanamid waste and ranged between 3.4 to 6.7 ppm and 8.7 to 21.7 ppm for the Du Pont and the Puerto Rican wastes, respectively. Dilution ratios of the waste in artificial seawater ranged up to  $32.63 \times 10^{-4}$ .

For the American Cyanamid waste mixtures, reflectance increased with increasing concentration at all wavelengths. For each mixture concentration, reflectance decreased as wavelength increased and generally leveled out at about 750 nm. No significant peaks or valleys were observed in the spectra at any wavelength for any of the concentrations. The slopes of the upwelled reflectance increased progressively at all wavelengths, but variably, with concentration.

The Du Pont waste mixtures and the Puerto Rican pharmaceutical waste mixtures did not produce upwelled signals significantly different from those of the base waters, which contained less than 4 ppm of suspended solids.

#### INTRODUCTION

The National Aeronautics and Space Administration (NASA), in cooperation with the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA), is conducting a research program to evaluate the feasibility of remotely monitoring ocean dumping of waste products such as sewage sludge and industrial wastes derived from diverse manufacturing processes. (See refs. 1 to 6.)

NOAA's National Ocean Survey (NOS) Ocean Dumping Program (ODP) has been developed to carry out monitoring and research studies on the effects of ocean disposal and to provide essential technical assistance to the EPA and the United States Army Corps of Engineers in their permit review, permit granting, and dump-site evaluation programs. These studies will help to assess the impact of present dumping activity and to provide a comparative base for future assessments. Eventually remote sensing may become a useful means to monitor movement, dispersion, and other effects of dumped material. Part of NASA's research involvement in the remote sensing research aspect of this effort is the measurement of upwelled spectral radiance and reflectance, both in the field (ref. 5) and in the laboratory (ref. 6).

Although the greatest volume of ocean dumping is of dredged material, the focus of the ODP up to this time has been on industrial wastes, in accordance with expressed EPA needs and the availability of funds. The industrial wastes studied in this report are dumped at the Deep Water Dump Site 106 (DWD 106) just southeast of the New York Bight apex and at a site 40 nautical miles north of Arecibo, Puerto Rico.

DWD 106 is located 106 nautical miles southeast of Ambrose Light and 90 nautical miles due east of Cape Henlopen, Delaware. The American Cynamid and the Du Pont (Graselli) plants in Linden, New Jersey, are two of the largest contributors to the waste disposed of at DWD 106. The American Cyanamid plant generates waste from the manufacture of about 30 different materials including rubber, paper and waste treatment chemicals, organophosphates, insecticides, intermediates, and surfactants. The Du Pont (Graselli) plant generates waste from the production of dimethylhydroxylamine (DMHA) and anisole.

The disposal site north of Arecibo is the dumping site used by a consortium of Puerto Rican pharmaceutical plants. The wastes include remains from the production of penicillin and other antibiotics and organic solvents.

Samples of waste from the Du Pont (Graselli) and the American Cyanamid plants and the consortium of Puerto Rican pharmaceutical plants were collected in February 1978 and brought to the NASA Langley Research Center. Here the wastes were mixed in various concentrations with artificial seawater in the marine upwelled spectral signature laboratory. Using as a light source the beam from a xenon arc lamp directed into the water by a mirror, a spectrometer mounted over the water tank measured upwelled spectral radiance from the various concentrations. Also, the radiance of the light source upwelled from a 99-percent diffuse reflector was measured and was used to calculate upwelled spectral reflectances for the concentrations. This report presents these data, along with beam attenuation coefficients and several physical and chemical parameters obtained from laboratory analyses.

#### SYMBOLS

- A area of spectrometer entrance slit, cm<sup>2</sup>
- D vertical displacement of oscilloscope measurement, cm
- $E(\lambda)$  spectral irradiance,  $\frac{W}{m^2-nm}$
- K ratio of instrument throughput A $\Omega$  to vertical-scale sensitivity factor S,  $\frac{\text{cm}^2-\text{sr}}{\text{mW/nm-cm}}$
- $L_{u}(\lambda)$  upwelled spectral radiance,  $\frac{mW/nm}{cm^{2}-sr}$

- $P(\lambda)$  spectral power, mW/nm
- S vertical-scale sensitivity factor, mW/cm-nm
- α beam attenuation coefficient, m<sup>-1</sup>
- λ wavelength, nm
- $\rho_{\mathbf{u}}(\lambda)$  spectral reflectance (relative to a 100-percent diffuse reflector), percent of input
- o standard deviation of instrument error
- $\Omega$  acceptance solid angle of spectrometer, sr

#### EXPERIMENTAL METHOD

Laboratory tests were conducted using the arrangement shown in figure 1. Major parts of the system include a water tank, circulation system, filtration and deionization system, solar simulator, first-surface mirror, and rapid-scan spectrometer. The light source is a 2.5-kW xenon short-arc lamp which produces a spectrum similar to that of the Sun. This setup is the same as that used in tests reported in references 2, 4, and 6. However, the irradiance from the solar simulator changed with use from what it had been in earlier tests. Figure 2 shows the normalized irradiance measured in past and present tests compared with the solar spectrum at a solar elevation angle of 30° (ref. 7). A more complete description of the laboratory equipment is given in the appendix.

Three laboratory tests were conducted to obtain upwelled radiance spectra for various concentrations of waste from the three sample sources. Twenty 1-gallon samples of each of the two industrial wastes were collected at the plants on February 16, 1978 (1 gallon = 3.79 liters). Samples of the pharmaceutical wastes that were dumped on February 6, 1978, were collected at Arecibo, Puerto Rico, on February 4, 1978, as the waste was being pumped from a holding tank to a barge. All of these samples were transported on ice in coolers to Langley Research Center and kept under refrigeration at 4°C until the tests were conducted.

Prior to testing each of the waste materials, the samples from an individual site were combined in a large vat and stirred with an electric outboard trolling motor. This is part of a standard procedure developed to ensure homogeneity among samples used in the subsequent tests. After stirring, a sample was withdrawn from the vat and was used in laboratory analyses to measure the chemical and physical parameters for each of the concentrates in tables I, II, and III.

For the upwelled radiance tests, artificial seawater was prepared according to EPA procedures (ref. 8). To prepare for an experiment, the water tank was filled to within 0.3 m of the top with 11 600 liters of conditioned tap water (filtered and deionized). While filling, various chemicals were added sequentially to the tank. A list of the chemicals and the amounts required are presented in table IV. The volumes of industrial wastes listed in tables I and II,

under "sample identification," were mixed with the water in each experiment to obtain the various "measured total suspended solids" and "calculated concentrations of waste added" shown in table I. Tables I and II also present the results of the base water analyses.

To obtain the first mixture of Du Pont waste in the water tank, a measured volume of waste was withdrawn from the vat into a graduated cylinder and then added to the water tank. Five additional increments were similarly withdrawn and added to the tank. The resulting mixtures were estimated to cover the range of dilution ratios likely to be observed at the ocean dump site. For the test of the American Cyanamid waste, the same volumes of American Cyanamid waste were similarly withdrawn and added to the water tank. The same procedure was followed for the test of the pharmaceutical waste, except that only five, rather than six, increments were added to the tank.

The laboratory analysis for total suspended solids was conducted by injecting a 1-ml sample into a preweighed crucible containing a glass-fiber filter. The liquid was pulled through the filter by suction. The crucible was heated to 82° C for 1 hour. After cooling, the crucible was reweighed and total suspended solids were calculated. Based on these calculations, the Du Pont waste (concentrate) contained 67.8 ppm of total suspended solids, the American Cyanamid waste contained 465 ppm, and the pharmaceutical waste contained 7340 ppm.

By using these values for measured total suspended solids, a water tank capacity of 11 600 liters, and the volumes of the increments used for mixing with the water in the tank, the values listed in table I as "calculated concentration of added waste" were calculated. These are the calculated accumulative total suspended solids in the water tank due solely to the addition of the six (or five) increments of waste. After each of the six (or five) increments was added to the water in the tank and the spectral signal measured, a sample was extracted from the tank. From each of these samples, seven (or six) in all, since a base-water sample was also taken, 1-ml samples were extracted and a laboratory analysis for total suspended solids was performed similar to that discussed previously. The "measured total suspended solids" resulting from these analyses are also listed in table I.

During testing, the circulation system was activated and the artificial seawater and later the mixtures were circulated without filtration. At the start of the experiment a radiance spectrum was measured of a plate painted with a 99-percent reflective paint (white card) placed near the surface of the water. The same measurements were made halfway through and at the end of the experiment to check for instrument drift. Also, these data were used with the radiance spectra for the various concentrations to obtain corresponding reflectance spectra. The circulation system remained on for the duration of the experiment.

After the white card measurements, an upwelled radiance spectrum for the base water was obtained. Then the first increment of industrial waste was mixed with the water in the tank to achieve the first mixture concentration. This mixture was allowed to circulate for a period of time (approximately 15 minutes) until the waste was evenly distributed throughout the tank. An upwelled radi-

ance spectrum was measured as before. The procedure was repeated to obtain upwelled spectra for the other concentrations. For the pharmaceutical waste experiment, after the spectral measurements were made for the mixtures, 20 ppm of Rhodamine WT dye (which is sometimes used as a tracer in ocean dump plume studies) was added to the final mixture and a spectral measurement was made. Generally, after the water tank was filled and seawater mixing completed, 2.5 to 3.0 hours were required to complete the test series for each material.

#### RESULTS AND DISCUSSION

When the values for calculated concentration of added waste listed in table I are added to the measured total suspended solids for the base waters, the sums are equal to theoretical total suspended solids. Comparisons of these values with the measured total suspended solids listed in the table are presented in figure 3. In all cases the measured values are higher than the theoretical values. For the American Cyanamid waste, chemical laboratory tests showed that precipitates are formed by the reaction of chemicals in the waste material with salts in the seawater. Similar precipitations may occur with the Du Pont and the pharmaceutical wastes, but to a lesser extent. The results presented in figure 3 show that the American Cyanamid waste produces a much greater amount of precipitate than do the Du Pont or the pharmaceutical wastes for the same volumes of added material. However, note that the Du Pont waste concentrate had measured total suspended solids of only 67.8 ppm.

Optical transmission measurements of the various concentrations were taken with a transmissometer that was lowered into the tank. This transmissometer has a wide band-pass filter with peak transmission at 510 nm. These transmission results are shown in figure 4.

Beam attenuation coefficient increased with increased waste material concentration for both the American Cyanamid and the Puerto Rican pharmaceutical materials. There was little change in the attenuation coefficient for the Du Pont waste. The fact that the beam attenuation coefficient was less than 1.0 for the base water of the Puerto Rican pharmaceutical tests tends to confirm the fact that the suspect laboratory-analysis values for total suspended solids shown in table I and in figure 3(c) were probably caused by contaminated containers and were not a property of the water. If base water concentration had been 17.0 ppm, beam attenuation coefficient probably would be in the range of 5 to 25 m<sup>-1</sup> based on unpublished test data with various materials.

Also shown in figure 4 are lower  $\alpha$  boundaries where the laboratory may not give accurate spectral reflectance data as discussed in the appendix. Because of this turbid-water limitation, reflectance spectra may not be accurate for the tests with (1) Du Pont wastes, (2) low concentrations of both American Cyanamid and pharmaceutical wastes, and (3) EPA seawater. In spite of this limitation, spectral reflectance data from these tests are shown for comparison purposes.

The data in figures 5 through 8 also show the effects of the greater amount of total suspended solids in the American Cyanamid waste mixtures compared with the Du Pont and the pharamceutical waste mixtures. Figure 5 presents data

obtained from the test of American Cyanamid waste in EPA seawater. Figure 5(a) presents the upwelled radiance as a function of wavelength for the EPA seawater and six mixtures of EPA seawater and American Cyanamid waste. Except for the two highest concentrations at about 850 nm, each addition of waste increased the upwelled radiance signal. The value at any particular concentration and wavelength is an average over the optical bandwidth. For example, values shown at 600 nm are averages of values from 584 to 616 nm (Spectral resolution = 32 nm). Measured total suspended solids for each mixture are indicated on the curves. Some of the variations in these data between 750 nm and 950 nm are caused by the spectral characteristics of the input xenon light source and are not believed to be related to the spectral response of the waste mixture. The discrepancy with the two highest concentrations at 850 nm is likely to be caused by an instrument or readout error. Figure 5(b) presents the upwelled radiance measured from the white card. It is a typical spectrum of the xenon arc lamp obtained in these tests, with prominent peaks and valleys in the 750- to 900-nm range and with generally increasing radiance from 480 to 750 nm. Upwelled radiance from the white card in earlier tests (such as those presented in ref. 4) showed similar peaks and valleys in the 750- to 900-nm range, but displayed a generally decreasing radiance from 480 to 750 nm. The radiance levels of the present tests were slightly higher than in reference 4. However, as shown in figure 2, the overall shapes of past and present spectra are not significantly different. Figure 5(c) presents upwelled reflectance calculated according to equation (5) in the appendix with the data from figures 5(a) and 5(b). As with the radiances, the reflectances increase with increasing concentration (increasing total suspended solids) except for the two highest concentrations in the region of the xenon peaks and valleys. The reflectances generally decrease from 400 to 750 nm. As noted previously, reflectance measurements for mixtures (1), (2), and (3) may not be accurate because of turbid-water limitations of the laboratory.

Figure 6 shows upwelled reflectances as a function of measured total suspended solids for several wavelengths for the American Cyanamid waste in EPA seawater. Upwelled reflectance varies nonlinearly with measured total suspended solids.

The upwelled spectral data for the Du Pont waste are presented in figure 7. As may be conjectured from the data in figures 3 and 4, the Du Pont waste mixtures have essentially the same upwelled radiances and reflectances as the base water. There were no consistent changes with additions of waste to the EPA seawater. Figures 7(a) and 7(c) present the bands in which the data fall. As discussed previously, these spectra are not considered accurate because of turbidwater limitations of the laboratory. Figure 7(b) presents the white card data used for calculating upwelled reflectances in this test. This curve is similar to the one shown in figure 5(b), but slightly higher.

The upwelled spectral data for the pharmaceutical waste are presented in figure 8. The reflectance results are similar to the results of the Du Pont test in that the waste concentration mixtures have essentially the same upwelled radiances and reflectances as the base water. There were no consistent changes with addition of waste to the EPA seawater. Figures 8(a) and 8(c) present the bands in which the data fall. These results are surprising because there is an appreciable increase in total suspended solids (fig. 3) and  $\alpha$  increases

to a value of 11 m<sup>-1</sup> (fig. 4) with increasing concentration of waste in the seawater. The lack of a stronger upwelled spectral signal may be because absorption of the particles or liquid counterbalances backscattering effects. Figure 8(b) presents the white card data used for calculating upwelled reflectances in this test. The curve is similar to the one shown in figure 5(b).

The radiance and reflectance spectra for the final pharmaceutical waste mixture with Rhodamine WT dye added are also presented in figures 8(a) and 8(c). These spectra have a sharp peak at about 600 nm which is a fluorescence feature characteristic of the Rhodamine WT dye. Also, in the visible range (400 to 700 nm) the spectra are higher overall for the mixtures with Rhodamine WT dye.

It should not be inferred from these results that an ocean dump plume of the pharmaceutical wastes cannot be remotely sensed. Unpublished multispectral scanner data obtained in an overflight of an actual ocean dump of the same material as was used in these laboratory tests but dyed with 20 ppm of Rhodamine WT showed little change in signal between the background water and the waste plume over most of the visible and near-infrared region of the spectrum. A small Rhodamine WT peak at 600 nm (similar to that in fig. 8) and a small decrease in signal at blue wavelengths was observed. However, in a prior flight experiment (ref. 9) over a different batch of the same material, strong changes in signal between the background water and waste plume were observed for undyed material. Subsequent laboratory measurements of transmission confirmed large changes in optical properties between various batches of the pharmaceutical wastes. An extensive research effort would be required to quantify the change in remote sensing signal that rely be expected from the Puerto Rican pharmaceutical disposal operations.

## CONCLUDING REMARKS

Radiance and reflectance spectra were measured for various dilution ratios of industrial wastes from the American Cyanamid and the Du Pont (Graselli) plants in Linden, New Jersey, and from a consortium of pharmaceutical plants in Arecibo, Puerto Rico. Also, beam attenuation coefficients and several other physical and chemical parameters obtained from laboratory analyses were presented.

Based on analyses of physical and chemical characteristics, beam attenuation coefficients, and upwelled reflectance spectra, the following conclusions are drawn:

- 1. For the American Cyanamid waste mixtures, reflectance at all wavelengths increased with increasing concentration. At each concentration, reflectance decreased as wavelength increased and generally leveled out (except for light-source-related peaks and valleys) at about 750 nm.
- 2. Tests of the Du Pont waste mixtures were significant in that there was little increase in total suspended solids and beam attenuation coefficient from that of artificial seawater for the dilution ratios tested. Beam attenuation coefficients remained so low that accurate measurements of reflectance could not be made because of turbid-water optical limitations of the system.

- 3. The pharmaceutial waste mixtures, similar to the Du Pont waste mixtures, did not produce upwelled signals significantly different from the upwelled signal for the base water, although measured total suspended solids and beam attenuation coefficients did indicate turbid-water conditions at high dilution ratios. Absorption of the particles and liquids may have counterbalanced back-scattering, so that no strong upwelled signal was measured. The upwelled signal for the final pharmaceutical waste mixture with Rhodamine WT dye added was higher overall in the visible range, compared with the signals from the mixtures without dye, and peaked strongly at about 600 nm, the characteristic peak for Rhoadamine WT dye.
- 4. All of the waste materials formed precipitates when added to EPA seawater. The American Cyanamid waste (concentrate) had more total suspended solids (465 ppm) than the Du Pont waste (concentrate) (67.8 ppm) and formed more precipitate when added to the EPA seawater than the Du Pont waste did. The pharmaceutical waste (concentrate) had the most total suspended solids of the three (7340 ppm) and formed an intermediate amount of precipitate when added to the EPA seawater compared with the other two wastes.

Langley Research Center National Aeronautics and Space Administration Hampton, VA 23665 August 13, 1979

#### APPENDIX

### LABORATORY AND EQUIPMENT

The cylindrical, steel water tank has a 2.5-m diameter and a 3-m depth. The bottom is concave as illustrated in figure 1. The tank interior is coated with a black phenolic paint that absorbs 97 percent of incident radiation over the spectral range of these measurements (400 to 980 nm). For these experiments, the tank was filled to within 0.3 m of the top with about 11 600 liters of water.

The circulation system was designed to maintain a vertically and horizontally homogeneous mixture in the tank and to maintain in suspension particles up to about 70 µm in diameter (specific gravity of 2.6). This particle size corresponds to fine sand. In order to accomplish these design goals, water is pumped from the drains at the bottom of the tank into a system of pipes which returns the water to the tank through two vertical pipes on opposite sides of the tank. The pipes empty just above the concave bottom. Forty-five degree couplings at the ends of the pipes direct the flow of the water counterclockwise over the concave bottom, creating a massive swirling motion of the water in the tank. Water and suspended particles generally rise near the periphery of the tank, are drawn through the vortex near the center, and return downward to the drains at the bottom. Tests using tracer techniques and transmission measurements have confirmed that this circulation system provides a near-uniform homogeneous mixture throughout the tank. For pollutants such as sewage sludge with specific gravities less than 2.6, the present laboratory setup can suspend particles larger than 70 µm in diameter.

The filtration and deionization system includes a commercial fiber swimming-pool filter, an activated carbon filter, and a charged resin deionizer. These units were placed in waterlines parallel to the main circulation system waterlines and can be used separately or in any combination by using valves. The two filters remove particulates and dissolved organic materials from the water before it reaches the deionizer where dissolved ionic substances are removed. After tap water is conditioned through this system, it contains less than 0.5 ppm of suspended solids and less than 2 ppm of dissolved substances.

The light source is a solar-radiation simulator designed to approximate the spectral content of the Sun's rays. The radiation spectrum is produced by a 2.5-kW xenon short-arc lamp and is transferred to the target plane through an optical arrangement inside the simulator and a collimating lens accessory. With the collimating lens accessory, the projected beam is collimated to a 0.15-m diameter, 0.3 m from the simulator, and has a ±2.5° collimation angle. For these experiments, the simulator was located approximately 6.0 m from the water tank as illustrated in figure 1. At this distance from the simulator, the beam is about 0.57 m in diameter. A mirror positioned 1.52 m above the water surface reflects the center of the beam to the water surface. The incidence angle with the water surface is 13° to avoid specular reflectance. The first-surface mirror is coated with aluminum and protected by an overcoat of silicon monoxide. It has a 0.3-m diameter and reflects an elliptical spot on the water surface which has a maximum diameter of 0.35 m. The simulator spec-

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tral input to the water surface is similar to, but not a precise duplicate of, sea-level standard solar-radiation curves often used in engineering calculations (ref. 7). Figure 2(a) shows that the standard sea-level curves are quite variable, depending on the solar elevation angle. Figure 2(b) shows the simulator spectrum normalized at 600 nm to the solar spectrum at a solar elevation angle of 30°. These curves suggest that when laboratory measurements are made at a 32-nm spectral resolution, the input spectrum and possibly the output measurements are similar to those that would be expected in the field if the solar elevation angle is on the order of 30°. The total intensity of the light hitting the water surface is approximately 8 percent of that in actual field conditions.

The rapid-scanning spectrometer system consists of a spectrometer unit with a telephoto lens attachment and a plug-in unit with an oscilloscope and camera attachment. The spectrometer unit with telephoto lens attachment is mounted 2.3 m above the surface of the water as illustrated in figure 1. The spectrometer uses a Czerny-Turner monochromator without an exit slit. The spectral output of the monochromator is focused on the target of a vidicon tube where the spectrum is stored as an electrical charge image. An electron beam periodically scans the vidicon target to convert the charge image into an electronic signal. This signal is processed by the plug-in unit which also functions as a controller between the spectrometer and the oscilloscope. The signal is displayed on the oscilloscope and is photographically recorded with a camera. The spectrometer is designed to measure power per spectral bandwidth (spectral power). The oscilloscope screen is used to show displacement of the instrument measurement. Oscilloscope displacement is proportional to spectral power, as shown in the equation,

$$D = \frac{P(\lambda)}{S} \tag{1}$$

The signal is internally processed in such a manner that the vertical-scale sensitivity factor S has a constant value over the wavelength range from 400 to 980 nm. Values of S were obtained by the manufacturer using calibration procedures described in reference 10. (After receipt of the instrument, the manufacturer's calibration was checked in an approximate manner prior to the tests described herein.) The upwelled spectral radiance  $L_{11}(\lambda)$  is defined as

$$L_{u}(\lambda) = \frac{P(\lambda)}{A\Omega}$$
(2)

where A is the area of the spectrometer entrance slit and  $\Omega$  is the acceptance solid angle of the spectrometer. Radiance values given herein are based on power received at the detector and are not corrected for losses through the telephoto lens. Tests with and without the lens indicate that such losses are much less than 5 percent for wavelengths between 400 and 980 nm.

Combining equations (1) and (2) results in

$$L_{\mathbf{u}}(\lambda) = \frac{\mathbf{DS}}{\mathbf{A}\Omega} \tag{3}$$

or

$$L_{u}(\lambda) = \frac{D}{K} \tag{4}$$

where

$$K = \frac{A\Omega}{S}$$

Thus, upwelled spectral radiance is determined from oscilloscope displacement and the proportionality constant K which is a function of the calibration factor S (which includes optical transmissivity) as well as acceptance angle  $\Omega$  and slit area A.

In order to obtain spectral reflectance  $\rho_u(\lambda)$ ,  $L_u(\lambda)$  measurements are made of a 99-percent horizontal diffuse reflector near the water surface. Values obtained are proportional to the spectrum being input to the water by the solar simulator. Reflectance is then computed by using the equation

$$\rho_{\mathbf{u}}(\lambda) = \frac{\left| \mathbf{L}_{\mathbf{u}}(\lambda) \right| \text{ Water mixture}}{\left| \mathbf{L}_{\mathbf{u}}(\lambda) \right| \text{ 99-percent diffuse reflector}}$$
(5)

By adjusting the slit area, spectral resolution of the spectrometer may be changed. For the tests described herein, all laboratory measurements were made with a spectral resolution of 32 nm.

The instrument has been observed to experience daily variations in the calibration factor K which affects absolute accuracy. According to instrument specifications, absolute accuracy of the measurements is believed to be ±20 percent in the 400- to 600-nm range and ±12 percent in the 600- to 900-nm range. (A comparison of results from a number of laboratory tests at NASA tends to verify the manufacturer's specifications.) Included in the absolute error is a repeatability uncertainty of ±13 percent in the 400- to 600-nm range and ±3.5 percent in the 600- to 900-nm range. Discussions with the manufacturer indicate that these values are believed to be representative of 30 error bands.

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Because of these absolute errors, spectral radiances from tests conducted on different days usually differ somewhat in magnitude. The overall shape of the relative spectrum over the wavelength range is consistent between tests conducted on different days.

Results from laboratory tests are always limited because the natural environment is not precisely duplicated. The effects of diffuse skylight, for instance, are not simulated in the laboratory used in this study. (The percent value of diffuse skylight to parallel sunlight varies from day to day in the natural environment.) However, calculations with quasi-single scattering and multiple scattering optical models (ref. 11) have indicated less than 1-percent difference in inherent reflectance between Sun-only and sky-only cases. For this reason, it is believed that inherent reflectance spectra measured in the laboratory are characteristic of those in the natural environment for the same water mixture.

Measurements of upwelled radiance for clear waters in this laboratory are considered questionable. Data tabulated in reference 12 suggest that beam attenuation coefficient  $\alpha$  should have a minimum value of 2.0 m<sup>-1</sup> before bottom reflection can be ignored when water depth equals 3.0 m. Reference 13 examined the effects of solar spot size and concluded that  $\alpha$  should have minimum values between 2.0 and 4.0 m<sup>-1</sup> to eliminate losses in signal when spot diameter is 0.3 m. Data from this laboratory for turbid water with  $\alpha$  greater than 4.0 m<sup>-1</sup> should be considered valid.

#### REFERENCES

- Hypes, Warren D.; and Ohlhorst, Craig W.: A Summary of the Test Procedures and Operational Details of a Delaware River and an Ocean Dumping Pollution Monitoring Experiment Conducted August 28, 1975. NASA TM X-74005, 1977.
- Usry, J. W.; Witte, William G.; Whitlock, Charles H.; and Gurganus, E. A.: Laboratory Measurements of Radiance and Reflectance Spectra of Dilute Primary-Treated Sewage Sludge. NASA TP-1038, 1977.
- Lewis, Beverley W.; and Collins, Vernon G.: Remotely Sensed and Laboratory Spectral Signatures of an Ocean-Dumped Acid Waste. NASA TN D-8467, 1977.
- Usry, J. W.; Witte, William G.; Whitlock, Charles H.; and Gurganus, E. A.: Laboratory Measurements of Radiance and Reflectance Spectra of a Dilute Biosolid Industrial Waste Product. NASA TP-1401, 1979.
- Johnson, Robert W.: Multispectral Analysis of Ocean Dumped Materials. NASA
  paper presented at the Eleventh International Symposium on Remote Sensing
  of Environment (Ann Arbor, Michigan), Apr. 25-29, 1977.
- 6. Whitlock, Charles H.; Witte, William G.; Gurganus, E. A.; and Usry, J. W.: Laboratory and Field Measurements of Upwelled Radiance and Reflectance Spectra of Suspended James River Sediments Near Hopewell, Virginia. NASA TP-1292, 1978.
- Moon, Parry: Proposed Standard Solar-Radiation Curves for Engineering Use.
   J. Franklin Inst., vol. 230, no. 5, Nov. 1940, pp. 583-617.
- Methods for Chemical Analysis of Water and Wastes. Rep. No. 16020, U.S. Environ. Prot. Agency, 1971.
- Johnson, Robert W.; and Ohlhorst, Craig W.: Application of Remote Sensing to Monitoring and Studying Dispersion in Ocean Dumping. Ocean Dumping of Industrial Wastes, B. H. Ketchum, D. R. Kester, and P. K. Park, eds., Plenum Press, 1979.
- 10. Stair, Ralph; Johnston, Russell G.; and Halbach, E. W.: Standard of Spectral Radiance for the Region of 0.25 to 2.6 Microns. J. Res. Natl. Bur. Stand., vol. 64A, no. 4, July-Aug. 1960, pp. 291-296.
- McCluney, W. R.: Ocean Color Spectrum Calculations. Appl. Opt., vol. 13, no. 10, Oct. 1974, pp. 2422-2429.
- 12. Whitlock, Charles H.: An Estimate of the Influence of Sediment Concentration and Type on Remote Sensing Penetration Depth for Various Coastal Waters. NASA TM X-73906, 1976.
- 13. Ghovanlou, A.: Radiative Transfer Model for Remote Sensing of Suspended Sediments in Water. NASA CR-145145, 1977.

TABLE I .- SUSPENDED SOLIDS IN CONCENTRATES AND ARTIFICIAL SEAWATER MIXTURES

Sample identification (dilution ratio)	Waste source	Calculated <sup>a</sup> concentration of added waste, ppm	Measured total suspended solids, ppm	Volatile suspended solids, ppm	
Artificial seawater American Cyanamid  (0) Du Pont  Puerto Rican pharmaceutical		0 0 0	2.3 3.4 b <sub>1</sub> 7.0	0.4 1.7 9.2	
1/3 gallon added waste (1.09 × 10 <sup>-4</sup> ) American Cyanamid Du Pont Puerto Rican pharmaceutical		0.05 .01 .60	9.2 4.6 8.7	5.7 3.1 6.5	
1 gallon added waste (3.26 × 10 <sup>-4</sup> ) American Cyanamid Du Pont Puerto Rican pharmaceutical		0.15 .02 2.40	11.6 4.2 b <sub>21.7</sub>	2.3 2.6 11.6	
2 gallons added waste (6.53 × 10 <sup>-4</sup> ) American Cyanamid Du Pont Puerto Rican pharmaceutical		0.30 .04 4.79	19.1 3.7 12.4	9.0 2.4 7.7	
4 gallons added waste (13.05 × 10 <sup>-4</sup> )	American Cyanamid Du Pont Puerto Rican pharmaceutical	0.61 .09 9.58	25.1 6.7 16.5	11.4 3.2 11.4	
7 gallons added waste (22.84 × 10 <sup>-4</sup> )	American Cyanamid Du Pont Puerto Rican pharmaceutical	1.06 .15 16.77	27.5 6.6 20.6	11.9 3.7 14.7	
10 gallons added waste (32.63 × 10 <sup>-4</sup> )	American Cyanamid Du Pont	1.52	29.9 4.2	15.1 3.0	
7 gallons added waste plus 20 ppm Rhodamine WT	Puerto Rican pharmaceutical		19.6	14.8	
Concentrate	American Cyanamid Du Pont Puerto Rican pharmaceutical		465.0 67.8 7340.0	424.6 21.8 1150.0	

 $^{\mathtt{a}}\mathtt{To}$  obtain theoretical total suspended solids concentration (fig. 3), add this column to measured values for base water.

bSuspect values of measured total suspended solids, probably caused by contaminated sample containers.

## TABLE II.- SOME PHYSICAL AND CHEMICAL PROPERTIES OF CONCENTRATES

## AND ARTIFICIAL SEAWATER MIXTURES

Sample identification		Concentration, ppm, of -					
(Dilution ratio)	Waste source	Chromium	Zinc	Lead	Nickel	Coppe r	Cadmium
Artificial seawater	American Cyanamid	<0.05		<0.05		2.20	<0.01
(0)	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05	<0.1 <0.05	.78 .23	<0.01 <0.01
1/3 gallon added waste	American Cyanamid	<0.05	0.34	<0.05	<0.1	2.10	<0.01
$(1.09 \times 10^{-4})$	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05		.99 .37	<0.01 <0.01
1 gallon added waste	American Cyanamid	<0.05		<0.05		2.10	<0.01
$(3.26 \times 10^{-4})$	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05		.97	<0.01 <0.01
2 gallons added waste	American Cyanamid	<0.05		<0.05		1.50	<0.01
$(6.53 \times 10^{-4})$	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05		.97 .32	<0.01 <0.01
4 gallons added waste	American Cyanamid	<0.05		<0.05		0.99	<0.01
(13.05 × 10 <sup>-4</sup> )	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05		1.00	<0.01 <0.01
7 gallons added waste	American Cyanamid	<0.05		<0.05		0.68	<0.01
(22.84 × 10 <sup>-4</sup> )	Du Pont Puerto Rican pharmaceutical	<0.05 <0.05		<0.05 <0.05		.93	<0.01 <0.01
10 gallons added waste	American Cyanamid	<0.05		<0.05		1.3	<0.01
(32.63 × 10 <sup>-4</sup> )	Du Pont	<0.05	.16	<0.05	<0.1	.92	<0.01
7 gallons added waste plus 20 ppm Rhodamine WT	Puerto Rican pharmaceutical	<0.05	0.15	<0.05	<0.05	0.42	<0.01
Concentrate	American Cyanamid	<0.05		<0.05		0.11	0.04
	Du Pont Puerto Rican pharmaceutical	0.11 <0.05		0.20 <0.05		0.62 <0.05	<0.01 <0.01

TABLE II.- Concluded

Sample identification (Dilution ratio)	Waste source	рĦ	Concentration, ppm, of -					
			copa	т	$\infty$ b	Oil and grease	Sulfate, SO <sub>4</sub>	Mercury
Artificial seawater	American Cyanamid	6.2	<250		6			<0.0001
(0)	Du Pont	7.3	<250	1	4	<10	2 500	<0.0001
	Puerto Rican pharmaceutical	7.5	<250		5	37		
1/3 gallon added waste	American Cyanamid	6.6	<250		4			<0.0001
$(1.09 \times 10^{-4})$	Du Pont	7.3	<250	1	6	<10	2 500	<0.0001
	Puerto Rican pharmaceutical	7.4	<250		7	27		<0.0001
1 gallon added waste	American Cyanamid	6.7	<250		6.5			<0.0001
$(3.26 \times 10^{-4})$	Du Pont	7.6	<250		4	<10	2 500	<0.0001
	Puerto Rican pharmaceutical	7.5	<250		10	15		<0.0001
2 gallons added waste (6.53 × 10 <sup>-4</sup> )	American Cyanamid	6.3	<250		8			<0.0001
	Du Pont	7.8	<250	1	6	<10	2 500	<0.0001
	Puerto Rican pharmaceutical	7.5	<250		12	19		<0.0001
4 gallons added waste	American Cyanamid	6.2	<250		11			<0.0001
$(13.05 \times 10^{-4})$	Du Pont	7.8	<250		6	<10	2 500	<0.0001
	Puerto Rican pharmaceutical	7.7	325		18	24		<0.0001
7 gallons added waste	American Cyanamid	6.2	<250		17			<0.0001
$(22.84 \times 10^{-4})$	Du Pont	8.1	<250		11	<10	2 500	<0.0001
,	Puerto Rican pharmaceutical	7.9	300		33	51		<0.0001
10 gallons added waste	American Cyanamid	6.3	<250		26			<0.0001
(32.63 × 10 <sup>-4</sup> )	Du Pont	7.9	<250		11	<10	2 500	<0.0001
7 gallons added waste plus 20 ppm Rhodamine WI	Puerto Rican pharmaceutical	7.9	350		33	88		0.0002
Concentrate	American Cyanamid	4.1	7 900	6 0	000			<0.01
	Du Pont	12.4	7 600	2 0		37.4	59 000	<0.0001
	Puerto Rican pharmaceutical		150 000	17 0	000	6300		0.006

aCOD - chemical oxygen demand. bTOC - total organic carbon.

TABLE III .- OTHER CHEMICALS IN THE CONCENTRATES

	Concentration, ppm, of -					
	Anisole	Toluene	Benzene	Xylene	Other hydrocarbons	Organic phosphates
American Cyanamid concentrate	0.05	900	1 50	0.5	1000	150 (3 compounds)
Du Pont concentrate	0.05	100	50	50	400	No trace

TABLE IV .- INGREDIENTS OF EPA ARTIFICIAL SEAWATER

	I ngr edient <sup>a</sup>	Amount required, b grams		
1	Sodium chloride	284	548	
2	Sodium sulfate	47	444	
3	Potassium chloride	8	120	
4	Sodium bicarbonate	2	320	
5	Potassium bromide	1	160	
6	Boric acid		348	
7	6-hydrated magnesium chloride	128	760	
8	6-hydrated strontium chloride		580	
9	Calcium chloride	13	456	
10	Sodium fluoride		35	

<sup>&</sup>lt;sup>a</sup>Listed in order of mixing sequence. <sup>b</sup>Based on a tank volume of 11 600 liters.

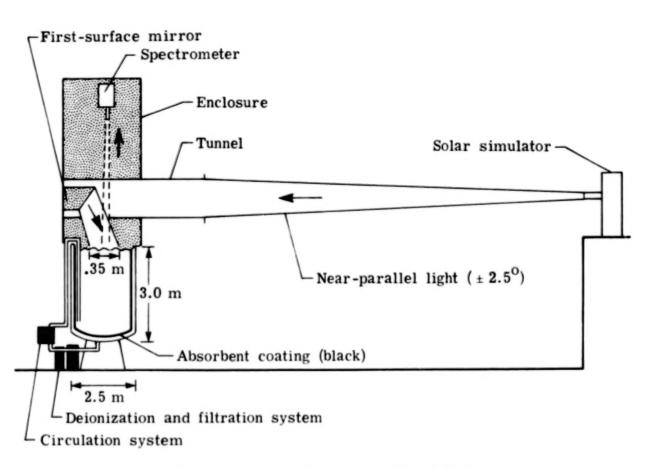
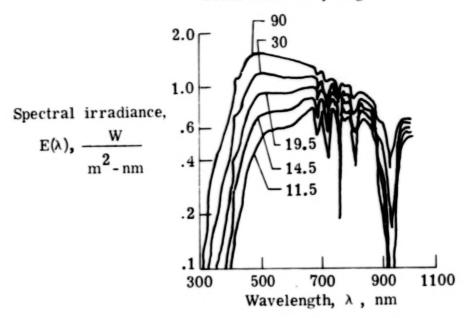


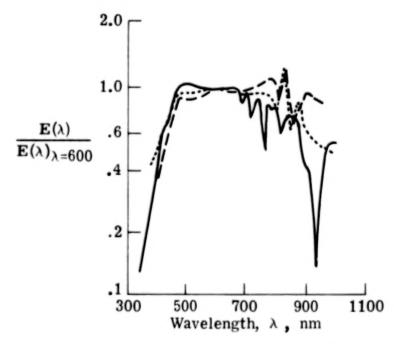
Figure 1.- Sketch of laboratory setup.

Solar elevation, deg



(a) Standard sea-level solar irradiance spectra (ref. 7).

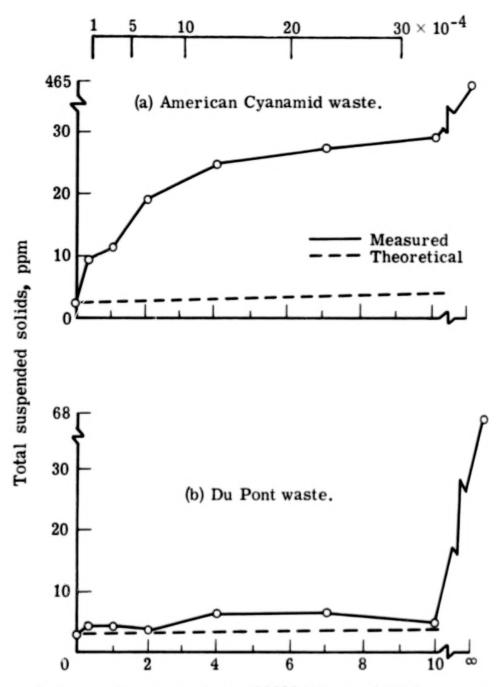
---- Solar simulator (32-nm spectral resolution) past tests
--- Solar simulator (32-nm spectral resolution) present tests
---- Solar elevation = 30°



(b) Solar simulator and standard sea-level spectra.

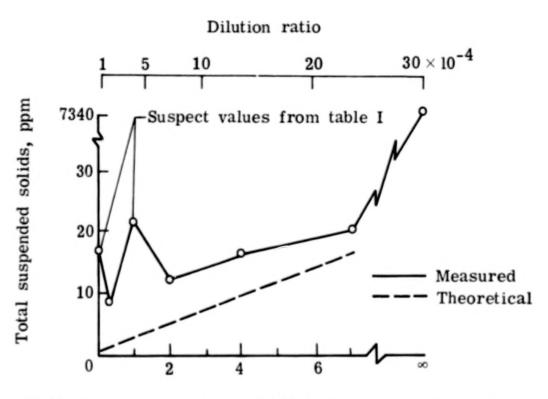
Figure 2.- Standard sea-level solar irradiance spectra and comparison with solar simulator data.

## Dilution ratio



Gallons of concentrate in 11600 liters of EPA seawater.

Figure 3.- Comparison of measured and theoretical total suspended solids.



Gallons of concentrate in 11600 liters of EPA seawater.

(c) Puerto Rican pharmaceutical waste.

Figure 3.- Concluded.

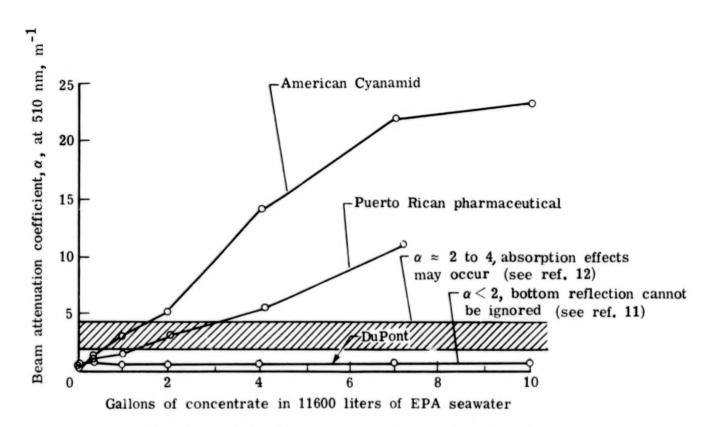
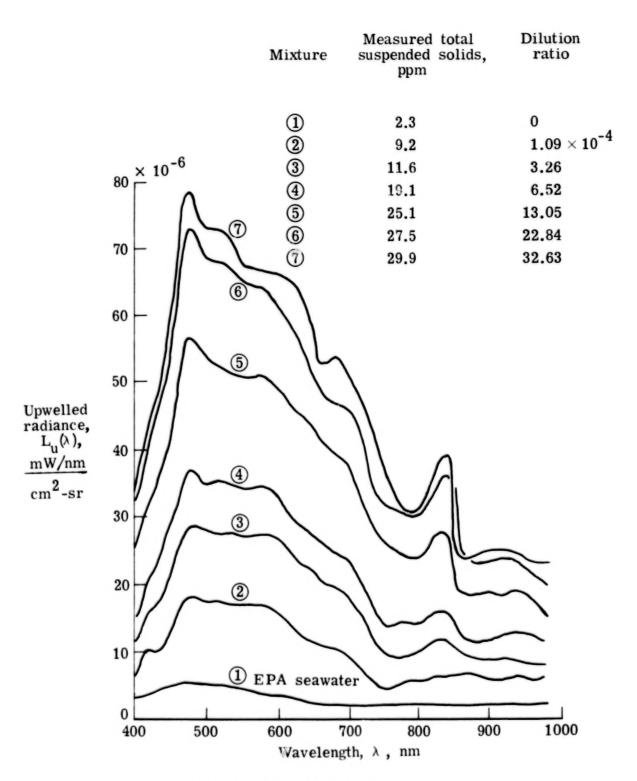
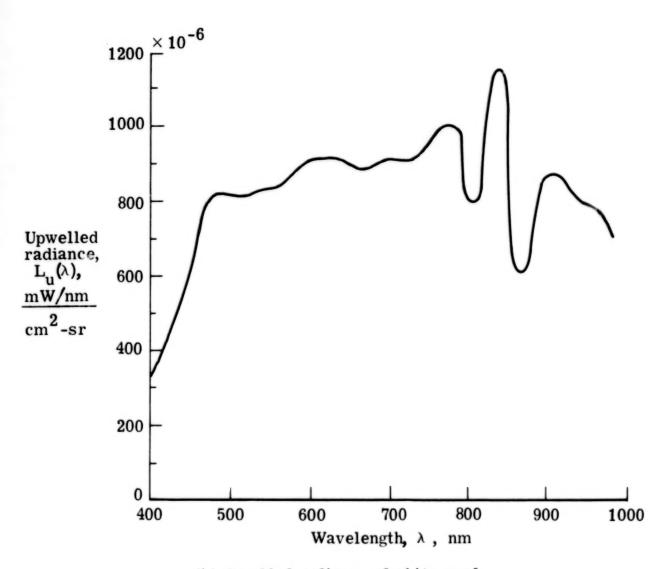


Figure 4.- Laboratory measurements of transmission.



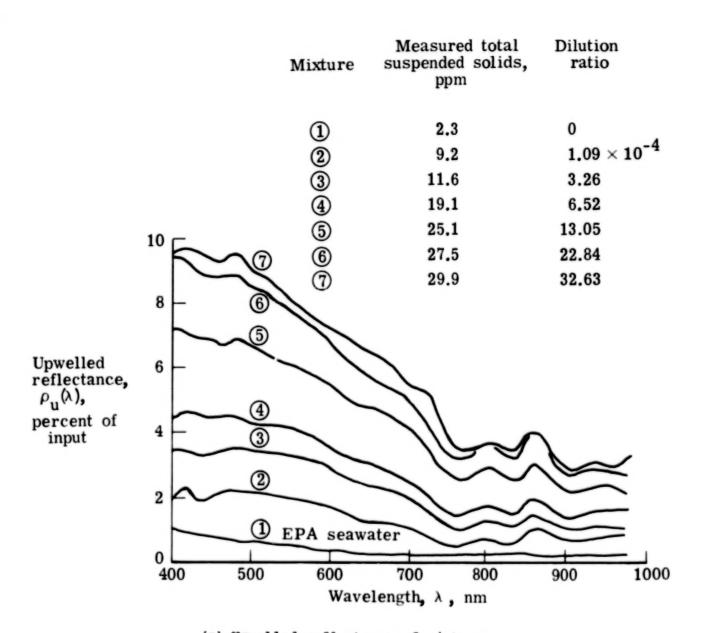
(a) Upwelled radiance of mixtures.

Figure 5.- Data obtained from the test of American Cyanamid waste in EPA seawater, March 28, 1978.



(b) Upwelled radiance of white card.

Figure 5.- Continued.



(c) Upwelled reflectance of mixtures.

Figure 5.- Concluded.

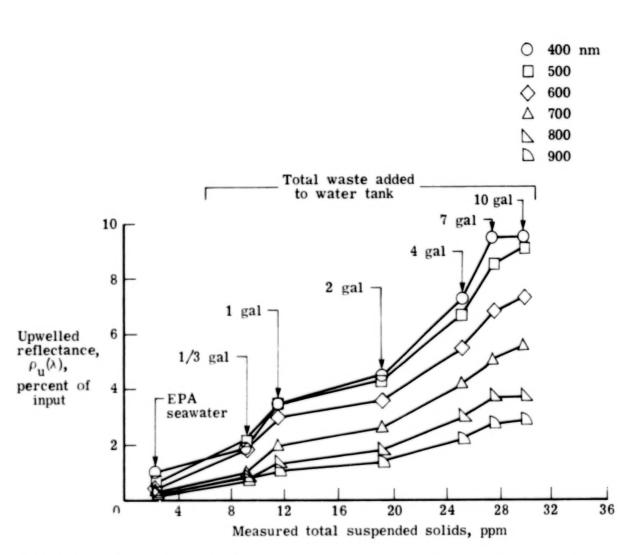
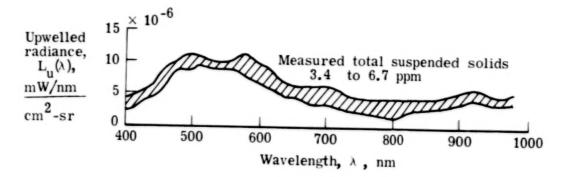
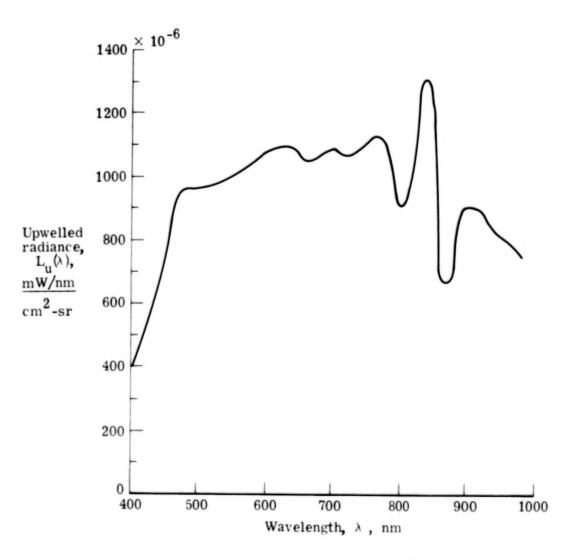


Figure 6.- Upwelled reflectance versus measured total suspended solids for American Cyanamid waste in EPA seawater, March 28, 1978.

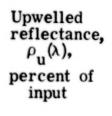


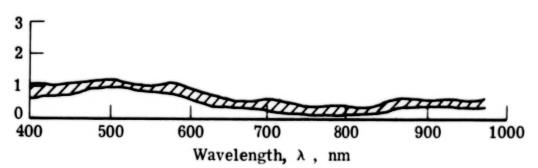
(a) Range of upwelled radiance of mixtures.



(b) Upwelled radiance of white card.

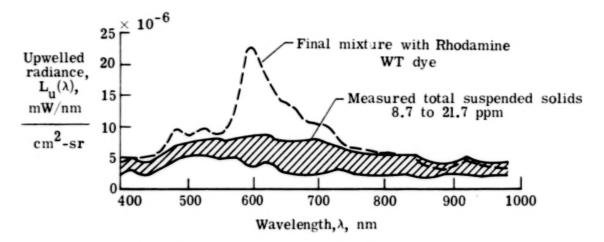
Figure 7.- Data obtained from the test of Du Pont waste in EPA seawater, March 14, 1978.



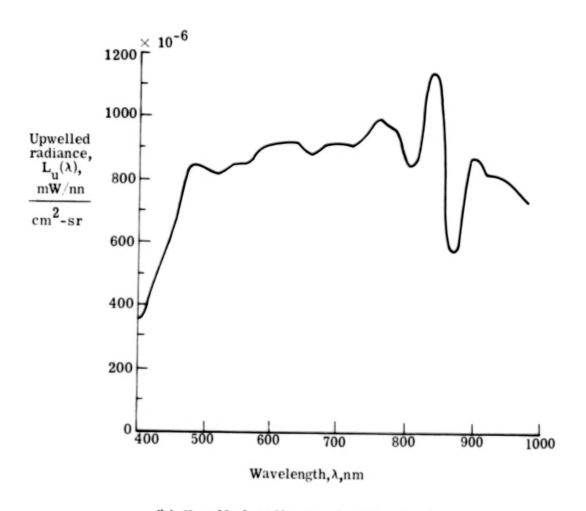


(c) Range of upwelled reflectance of mixtures.

Figure 7.- Concluded.

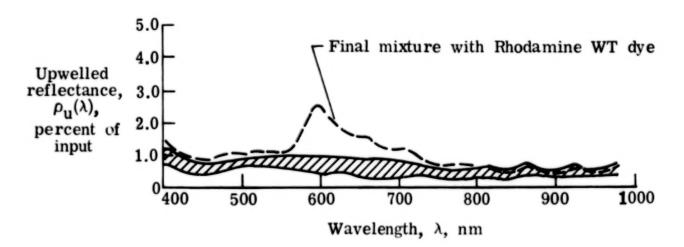


(a) Range of upwelled radiance of mixtures.



(b) Upwelled radiance of white card.

Figure 8.- Data obtained from the test of Puerto Rican pharmaceutical waste in EPA seawater, May 10, 1978.



(c) Range of upwelled reflectance of mixtures.

Figure 8.- Concluded.

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